Some geochemical consequences of environmental change and human activity in Nova Scotia, Canada

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Synopsis

Geochemical and environmental surveys have outlined examples of potential and actual environmental impacts in the Cobequid Highlands and Meguma zone regions of Nova Scotia, Canada. The synergy of exploration and environmental methodologies enables the identification of important chemical reactions within present-day and immediately post-glacial ecosystems in Nova Scotia. Cores taken in lake sediments define geochemical baselines for the modern and pre-industrialization periods. The investigation of lake and stream drainage systems indicates the presence of numerous chemical and organic factors that can be attributed to man's activities, such as construction and energy consumption.

Geochemical surveys of lake and stream sediments are used to locate potentially toxic, high-risk areas in Nova Scotia, including areas of elevated U and Mo in the Cobequid Highlands and As and Sb around Lunenburg. Changes in pH are due to the progressive acidification of drainage systems. The increasingly abundant protons are carried by either acidified precipitation or drainage, which can subsequently produce significant changes in levels of toxic heavy metals in surficial materials. Urban development around Halifax has given rise to several environmental modifications, which are recorded in modern sediments in lake catchments. Case studies provide detail of climatic change after the Ice Age and of the effect of human settlement and industrialization in the catchments of the Chocolate, Soldier and Five Island Lakes.

Man-made chemical influences are present in Nova Scotia and must be recognized when planning mineral exploration programmes. Rapid change occurs in most surface drainage systems in Nova Scotia, with the possibility of numerous chemical reactions taking place. Spatial and temporal variations in the chemistry of modern and recent sediments are of interest to exploration and environmental surveys.

In Nova Scotia most surveys for mineral exploration and environmental geochemistry have traditionally been conducted as separate areas of endeavour with little operational overlap. Nova Scotia is, by Canadian standards, a small province with approximately 970 000 people inhabiting an area of about 53 000 km^2. The economy is essentially resource-based, the principal emphasis being on fishing, forestry, agriculture, mining and manufacturing. Since the mid-1950s expanding industrialization has provided the impetus for increased exploration to find new mineral resources to sustain economic development. At approximately the same time environmental concerns focused initially on acid precipitation, but, more recently, the issues have reflected a developing awareness of the chemical consequences of changing land use. It is the aim of the present contribution to identify chemical factors of

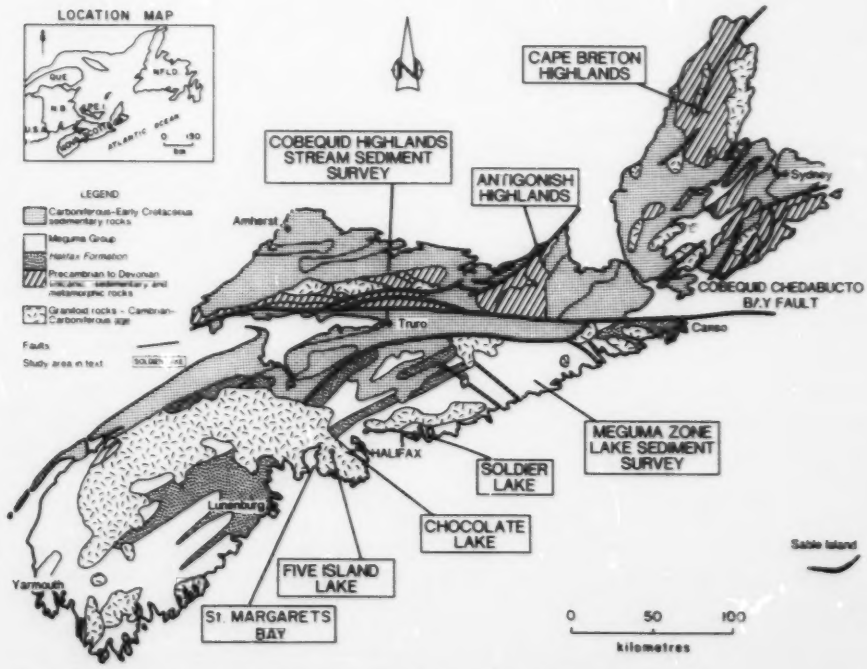

Fig. 1 Simplified geological map of Nova Scotia with locations of study areas

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common concern to environmental and exploration geochemistry, as indicated by recent work in both disciplines in Nova Scotia (Fig. 1).

In Nova Scotia environmental and exploration geochemical studies have generated extensive databases of chemical and biological information. Since 1956 mineral exploration has been conducted using lakes, streams, soils, bedrock, tills and plants in various regions of the province.[1] Most environmental studies have concentrated on acid precipitation,[2-6] but more recently there has been an added focus on acid drainage and intra-coastal pollution.[7,8] Acidification and fumigation by oxides of nitrogen and sulphur as well as by organic molecules are affecting the mobilization and sequestration of the geochemical components of ecosystems. All this information indicates a significant man-made (anthropogenic) component in the chemical budgets found in Nova Scotia. The chemical data compiled by the two disciplines can be used in a complementary fashion to estimate some of these components and how they behave in the surficial environment.

Study areas

In 1983 a regional stream-sediment survey using 'standard' 80-mesh sieved samples was conducted throughout the Cobequid Highlands (Fig. 1). The Highlands consist of an upland core of Precambrian and lower Palaeozoic rocks surrounded by lowlands of Upper Carboniferous and younger rocks. The southern boundary is the east-trending Cobequid–Chedabucto Bay fault system.

In the early 1970s and 1980s detailed limnological studies[9-12] and lake-sediment exploration geochemistry[13,14] were also completed in the Meguma zone (Fig. 1). The Meguma zone is underlain by Meguma Group metasediments of Cambro-Ordovician age, which are intruded by 370-m.y. old (Devonian to Carboniferous) granitoid rocks. The Meguma Group is subdivided into two main formations, the upper Goldenville psammite and lower Halifax slate (pelite). Detailed lake studies in the Meguma zone were carried out in the lake systems indicated in Fig. 1. Five Island Lake is the main headwater lake of a chain of lakes in the St Margarets Bay area that includes Hubley Big Lake and Long Lake. Soldier and Chocolate Lakes are located near Halifax, which is the main metropolitan area of Nova Scotia. The lake basins or catchments can be covered by till to a depth of several metres.

Methods

The exploration geochemical samples were collected from lakes and streams using field sieving (–1 mm) for streams and helicopter grab sampling for lakes.[1] In the lake studies sediment–water interface samples from short piston cores (coring drives were initiated 10–40 cm above sediment and penetrated 40–80 cm into sediment) were collected near defined inlets and outlets. Samples of surface water were collected at lake inlets and outlets. Lake bathymetry was compiled using a boat-mounted sounder. All water and sediment samples were analysed for major ions and heavy metals at the environmental chemistry laboratory of Victoria General Hospital, Halifax, and various commercial laboratories, including facilities of the Geological Survey of Canada.[1] At each lake coring station a sub-sample was taken with a 1.0-cm^3 volumetric piston sampler.[15] The sub-samples were placed in snap-cap vials before processing for dry and ash weight determinations and analysis of microfossils. Long sediment cores were recovered using a modified Livingstone piston sampler[16] in contiguous 1.0-m segments. Core segments were sealed in the field and returned for storage at the laboratory. Sediment density and the organic matter content were determined on the sub-samples of sediment

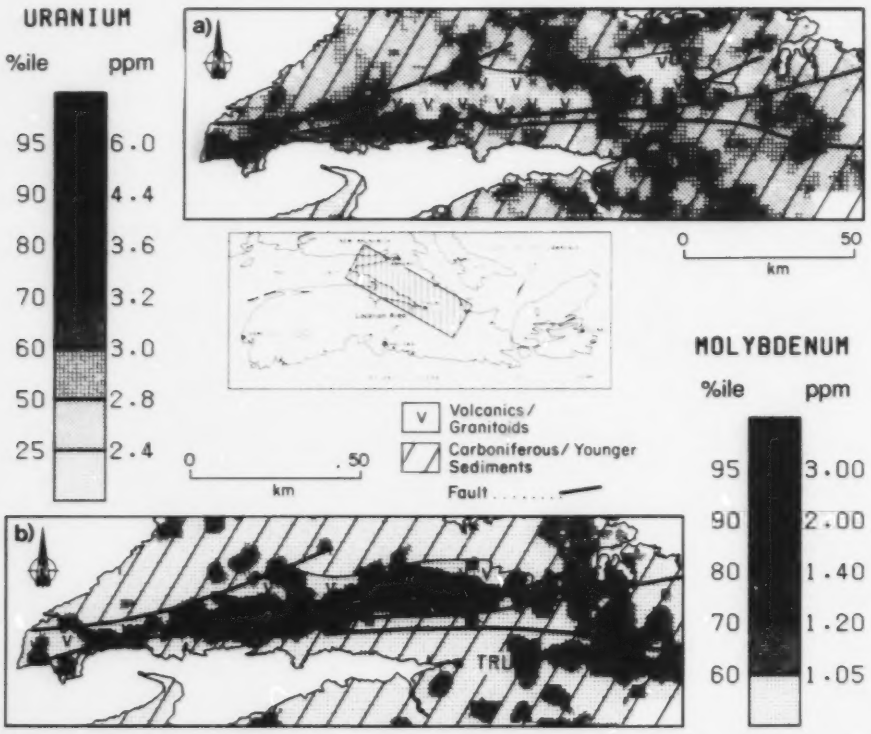

Fig. 2 Computer-generated contour plots for (*a*) uranium and (*b*) molybdenum in stream sediments from Cobequid Highlands of Nova Scotia

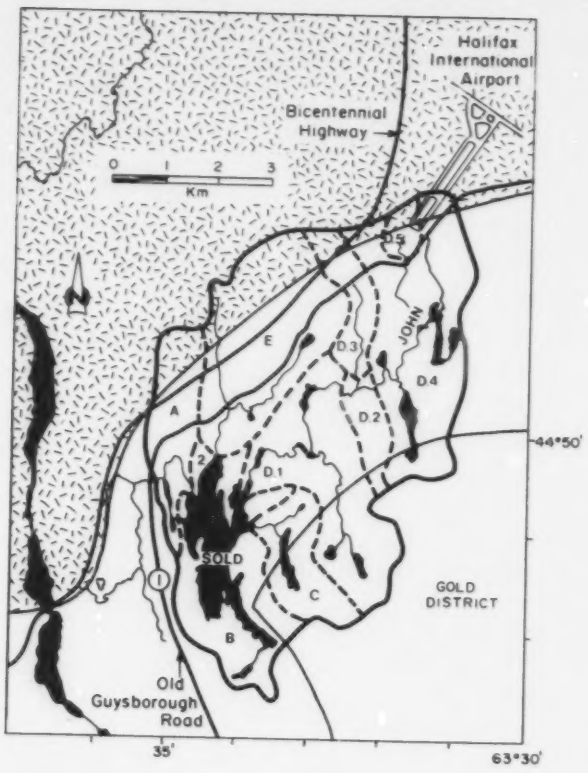

Fig. 3 Soldier Lake: location map showing principal subwatersheds. (After Ogden and Rogers[11])

cores. Cores were sealed in plastic stretch wrap after sampling and archived at 5°C.

The organic matter in lake-sediment samples was determined from the loss on ignition (450°C for >6 h) from oven-dried sub-samples that had been ground to pass a 100-mesh screen (1.0 cm^3 at 105°C for 24 h). A combination of methods was used for chemical analysis, including atomic absorption, neutron activation and inductively coupled plasma.[1,12,14] The preparation of samples for microfossil analysis followed standard procedures[16] and involved wet sieving at 125 μm, deflocculation in 10% KOH, demineralization in 48% HF, acetolysis (9:1 acetic anhydride–concentrated sulphuric acid mixture) for pollen and digestion in H_2O_2 (30%) and concentrated H_2SO_4 for diatoms.

Results

Changes in pH

Changes in pH have the greatest potential effect on the surficial environment in Nova Scotia. Most recent attention has been focused on external acidification.[17] Lately, the potential risk of toxic poisoning from an increased mobilization of heavy metals due to pH change has been receiving more attention.[18]

Mobilities of heavy metals

Application of catchment basin analysis for anomaly recognition and background characterization to the Cobequid Highlands regional stream-sediment and water samples quantified variance due to lithology and secondary scavenging by Fe and Mn.[19] In the Cobequid Highlands stream catchments on granitoid and volcanic rocks contain elevated background levels of most heavy metals, including Zn, Cu, Pb, As, Mo and U. Contour plots of U and Mo (Fig. 2) illustrate the elevated background levels that are

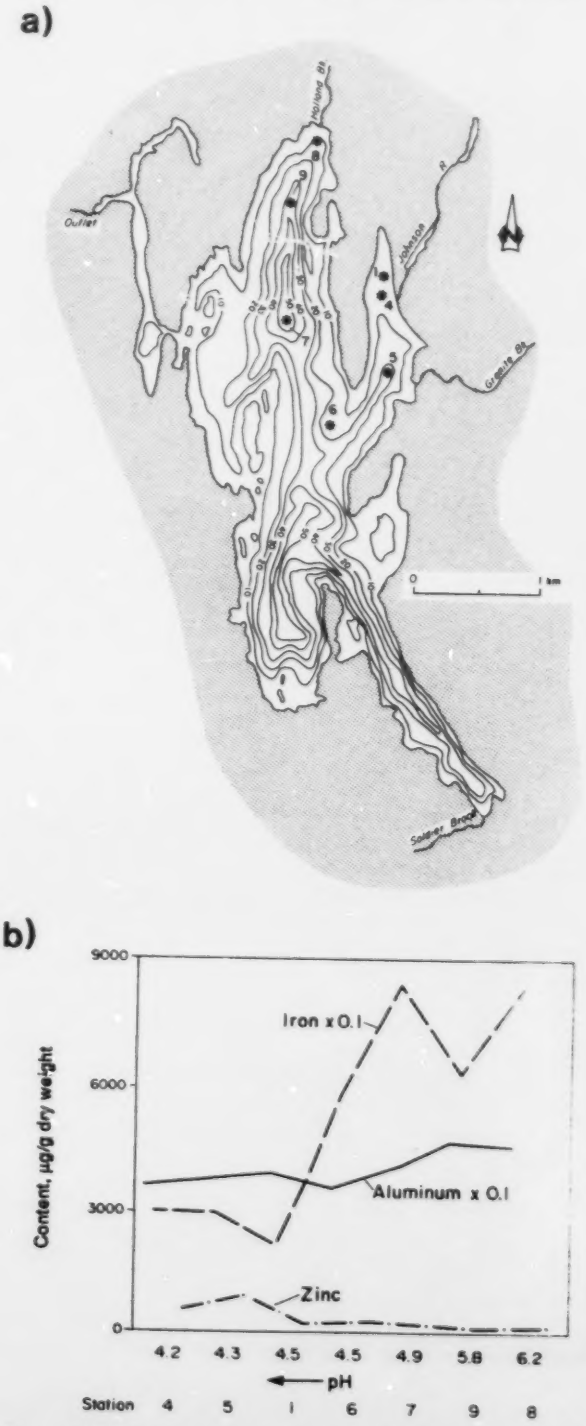

Fig. 4 Soldier Lake: (*a*) sample location map and (*b*) geochemical gradients present in samples from sediment–water interface. (After Ogden and Rogers[11])

Fig. 5 Location of sample sites for detailed study of lakes of St Margarets Bay area near Halifax, Nova Scotia. (See Rogers[13] for details related to gold and heavy minerals in lake sediment from this area)

found in stream catchments containing the volcanic and granitoid units. Both U and Mo have very limited mobility in Cobequid Highlands surface waters, which have a pH in the range 6.2–6.7. Phase studies[20,21,22] of Mo solubility indicate that insoluble complexes form in the presence of iron and of organic and dissolved material, all of which are present in the stream sediment and water in this area.[1]

Geochemical solute and hydrogen ion (proton) budgets

The progressive acidification of lake systems in Nova Scotia since the end of the second world war has been noted in numerous studies.[2–6] Geochemical gradients related to pH were detected in 1987 in lake-bottom sediment samples from Soldier Lake (Fig. 3).[11] The Soldier Lake catchment contains only Meguma Group rocks (Fig. 3). In the 1987 study nine water samples were taken from just above the sediment–water interface below the main upstream inlets in the northern part of the lake system (Fig. 4(*a*)). Stations (Fig. 4(*a*)) below the Johnson River inlet show acidic pH from 4.2 to 4.5 with a corresponding drop in Fe and Al and with higher Zn, which is believed to indicate a mobility barrier that is related to differing pH in the sedimentary column of the lake bottom (Fig. 4(*b*)). The Holland Brook inlet shows a more basic profile, with pH from 4.9 to 6.2 and increased Fe and Al and lower Zn compared to the Johnson River inlet. The increased hydrogen ion concentration and acidic pH values of around

Table 1 Hydrological data for lake system of St Margarets Bay area

Lake	Catchment size, km²	Surface area, ha	Mean depth,* m	Water residence, months	Flushing rate, years
Five Islands	21.3	143	3.6	4	4.8
Big Hubley	36.7	253	2.9	2	5.1
Long	46.6	70	2.8	2	25.4

Mean depth calculated as volume/area.

Table 2 Water chemistry data for lakes of St Margarets Bay area

Location	pH	Cond. $\mu S\ cm^{-1}$	Colour, Pt–Co	Na, mg/l	K, mg/l	Ca, mg/l	Mg, mg/l	Al, mg/l	Fe, mg/l	Mn, mg/l	HCO_3, mg/l	Cl, mg/l	S, mg/l	DOC, mg/l	CSI	Date
010 SL-OUT	4.90	70.80	20.00	8.00	0.33	2.50	0.55	0.27	0.15	0.18	0.00	14.00	8.60	1.52	–4.66	30/5/87
011 FIL-1	5.60	62.70	55.00	8.60	0.35	1.70	0.43	0.33	0.32	0.07	0.00	15.00	5.00	3.81	–3.77	31/5/87
012 HUB-1	5.10	44.10	55.00	5.90	0.23	0.80	0.33	0.22	0.36	0.03	0.00	9.40	3.70	3.81	–4.68	31/5/87
013 LL-1	5.30	40.10	55.00	5.20	0.20	0.78	0.32	0.17	0.19	0.02	0.00	8.10	3.70	3.81	–4.50	31/5/87
014 LL-OUT	4.80	41.40	55.00	5.20	0.20	0.67	0.32	0.17	0.12	0.03	0.00	8.20	3.50	3.81	–4.90	31/5/87
101 FIL-1	4.52	115.70	50.00	18.00	0.73	2.40	0.85	0.23	0.39	0.05	0.00	29.00	9.00	5.40	–4.85	19/9/87
102 FIL-2	5.12	89.00	70.00	12.00	1.20	3.00	0.83	0.26	0.57	0.05	2.90	15.00	15.20	6.71	–3.58	19/9/87
103 FIL-3	4.65	49.30	50.00	8.90	0.31	0.86	0.42	0.10	0.20	0.03	0.00	10.00	5.20	5.40	–5.03	19/9/87
104 FIL-4	4.84	82.30	15.00	9.30	0.40	1.20	0.51	0.14	0.15	0.03	0.00	13.00	4.50	3.11	–4.75	19/9/87
105 FIL-5	5.05	62.30	17.50	9.30	0.42	1.20	0.52	0.17	0.15	0.05	0.00	13.00	4.50	3.28	–4.53	19/9/87
106 HUB-1	4.82	59.20	40.00	8.20	0.31	1.10	0.52	0.20	0.56	0.07	0.00	11.00	5.50	4.75	–4.76	19/9/87
107 HUB-2	4.80	64.80	70.00	9.00	0.31	1.30	0.61	0.21	0.44	0.04	0.00	14.00	4.00	6.71	–4.91	19/9/87
108 HUB-3	4.61	36.10	87.50	3.80	0.23	0.81	0.48	0.36	0.11	0.00	0.00	2.20	7.00	7.85	–5.01	19/9/87
109 HUB-4	4.76	46.30	75.00	6.00	0.31	0.77	0.46	0.23	0.15	0.00	0.00	8.90	5.50	7.04	–4.88	19/9/87
110 HUB-6	4.95	45.00	15.00	6.20	0.33	0.83	0.40	0.13	0.08	0.03	0.00	8.50	3.80	3.11	–4.75	19/9/87
111 HUB-5	4.78	45.20	15.00	6.20	0.38	0.72	0.33	0.23	0.07	0.00	0.00	9.20	4.50	3.11	–5.00	19/9/87
201 FIL-1	4.60	118.50	100.00	13.00	0.54	2.30	0.85	0.33	0.50	0.08	2.50	25.00	6.50	8.67	–4.15	10/10/87
202 FIL-2	5.00	117.60	150.00	14.10	1.30	3.60	0.36	0.43	0.36	0.08	3.70	23.00	15.00	11.94	–3.96	10/10/87
203 FIL-3	4.60	54.70	40.00	6.10	0.24	0.98	0.47	0.15	0.12	0.05	0.00	12.00	5.40	4.75	–5.03	10/10/87
204 FIL-4	4.90	63.20	15.00	7.50	0.33	1.20	0.51	0.10	0.14	0.06	0.00	15.00	5.40	3.11	–4.69	10/10/87
205 FIL-5	5.00	62.20	17.50	7.50	0.31	1.20	0.51	0.08	0.12	0.06	0.00	14.00	4.50	3.28	–4.59	10/10/87
206 HUB-1	4.80	62.60	20.00	8.10	0.36	1.20	0.51	0.07	0.10	0.06	0.00	15.00	4.50	3.44	–4.79	10/10/87
207 HUB-2	4.70	67.20	50.00	8.20	0.33	1.30	0.55	0.11	0.15	0.06	0.00	15.00	5.40	5.40	–4.86	10/10/87
208 HUB-4	4.70	47.70	60.00	5.50	0.26	0.80	0.44	0.17	0.13	0.03	0.00	9.40	5.40	6.06	–4.96	10/10/87
209 HUB-5	4.80	44.50	17.50	5.30	0.29	0.79	0.41	0.08	0.10	0.05	0.00	9.60	5.40	3.28	–4.79	10/10/87
210 LL-1	4.70	47.80	30.00	5.00	0.29	0.78	0.42	0.12	0.10	0.04	0.00	9.40	1.10	4.09	–4.98	15/10/87
211 LL-2	5.40	22.70	20.00	2.60	0.29	0.63	0.37	0.05	0.04	0.02	2.50	4.10	1.80	3.44	–3.71	15/10/87
212 LL-3	4.90	40.60	50.00	5.00	0.29	0.80	0.42	0.13	0.17	0.04	1.80	8.50	1.80	5.40	–4.30	15/10/87
213 LL-4	4.90	40.90	50.00	4.90	0.26	0.77	0.41	0.12	0.17	0.04	0.00	8.30	4.20	5.40	–4.79	15/10/87

Cond., conductivity; DOC, dissolved organic carbon; CSI, calcite saturation index.
SL, Soldier Lake; FIL, Five Island Lake; HUB, Hubley Big Lake; LL, Long Lake.
Note: fish reproduction is affected when pH falls below 5.0.

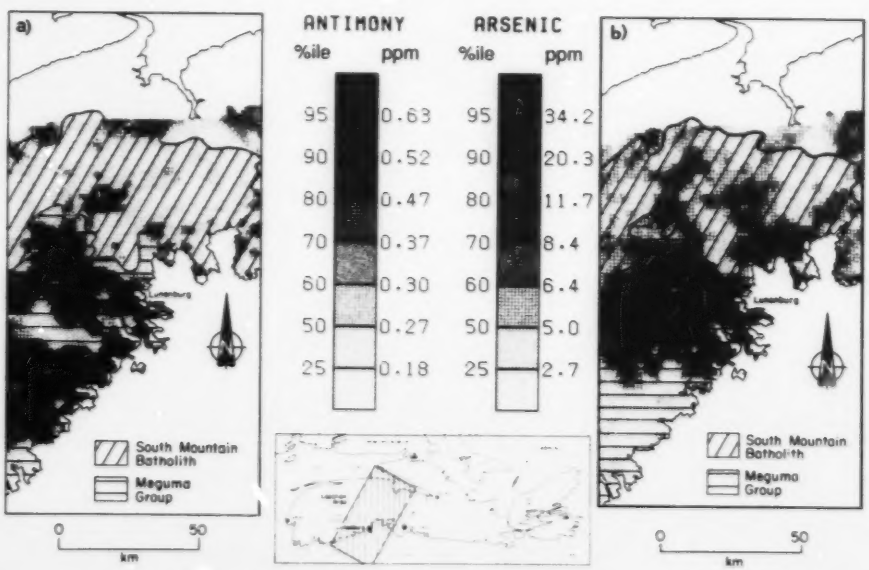

Fig. 6 Computer-generated contour plots for (*a*) antimony and (*b*) arsenic in lake sediments from Meguma zone, southwestern Nova Scotia

4.5 are attributed to a build-up of excess protons from acidified drainage caused by the oxidation of pyritic slate exposed during the construction of an airport runway in the Johnson River sub-watershed of Soldier Lake.[11] Subsequent sheet-creting (cement, fly ash, polypropylene fibre) of the exposed bedrock has prevented further proton imbalance and the gradients in Soldier Lake were not detected by repeat sampling in 1990. The pH of outlet water has also increased by approximately 0.5 pH units.[22a]

In the St Margarets Bay area (Figs. 1 and 5) increased

external acidification was detected during sampling of lake-surface water. In 1987 the pH ranged from 4.8 to 5.6, compared to a range of 6.0 to 6.3 in 1979.[23,24] This progressive acidification of lakes is consistent with patterns noted by Bricker in New England[17] (northeastern U.S.A.) and by Watt and co-workers[2] and by Freedman and Ogden[32] in Nova Scotia.

The areal and limnic parameters of the catchments of the St Margarets Bay lakes are shown in Table 1. Differences in the water chemistry that are apparent in Table 2 reflect high-flow spring runoff prior to the onset of evapo-transpiration and low flow in September following seasonal evapo-transpirational stress; recharge, seen in the October samples, reveals changes in the ionic loading of the lakes, which is closely related to their hydrology. The lakes flush several times a year and are generally polymictic with no pronounced thermal stratification. As a result of this flushing, Eh values at the mud–water interface rarely fall below 300 mV.

The concentrations of elements and compounds in outlet water are stable despite seasonal hydrological differences, although the chemistry of the inlet water varies as it reflects different vegetational and geological substrates in the individual sub-watersheds (Table 2). Colour may be used as a surrogate for DOC (dissolved organic carbon) according to the formula DOC = 0.213 × Colour − 77.0.[23] The amount of organic anion (A^-) available to complex with polyvalent metal cations (especially Al and Fe) is estimated using equations developed by Oliver and co-workers.[24] DOC values range from 3.1 to 5.4 mg/l at the outlets and inlet values range from 3.1 to 11.9 mg/l. In general, organic anions (as meq/l) contribute less than 5% of the ion sums and have a negligible effect on cation–anion balances.

Table 3 Flow data for lakes of St Margarets Bay area, 1987

Date	m^3/sec	m^3/ha
31 May	0.295	9.47
9 Sept	0.058	1.86
10 Oct	0.561	17.99

Source: Water Survey Canada.

Quite low calcite saturation index (CSI) values of less than −3.0 represent an increasing threat to the reproductive success of fish, especially salmonids, and indicate that lake hydrogeochemistry may become increasingly oligotrophic as acidification continues. Outlet pH values are characteristically slightly higher than most of the inlet values, implying at least some seasonal alkalinity in the lakes. Runoff on sampling days was used to explore downstream mass flow relationships for chloride, aluminium, iron and manganese (Table 3). Because chloride does not form insoluble precipitates, it is generally used as a mass flow tracer,[9,25,26] and loading may be expected to increase downstream as tributary watersheds contribute to system loading. This is shown in Tables 3 and 4 for all three sampling dates, and is generally true for manganese—similar to its behaviour in Soldier Lake.[9] Aluminium and iron appear to be more variable, but mass flow generally appears to increase downstream. It does not seem that any of the St Margarets Bay lakes are serving as major geochemical sinks. This is in contrast to Soldier Lake,

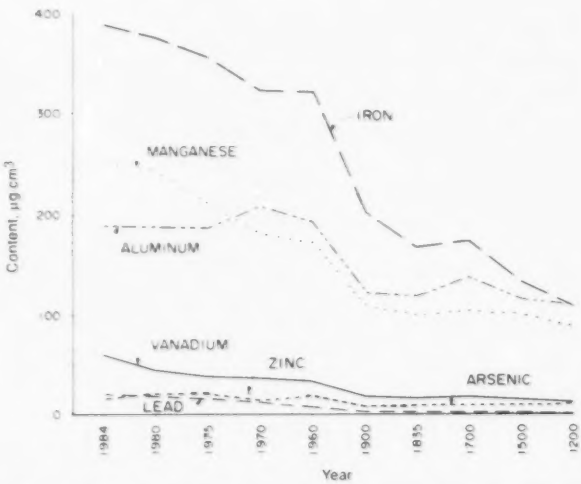

Fig. 7 Plot of content of selected heavy elements in lake-sediment borehole, Chocolate Lake, showing changes with time

Table 4 Mass balance data for lakes of St Margarets Bay area, 1987 (for flows see Table 3)

Source	Area, ha	Output (10^6 l)			Ion	Concentration, mg/l			Mass flow, kg		
		31 May	9 Sept	10 Oct		31 May	9 Sept	10 Oct	31 May	9 Sept	10 Oct
FIL-IN*	1186	11.2	2.2	21.3	Cl	—	10	12	—	22	255.6
					Al	—	0.1	0.15	—	0.22	3.195
					Fe	—	0.2	0.12	—	0.44	2.556
					Mn	—	0.03	0.05	—	0.066	1.065
FIL-OUT	2258	21.4	4.2	40.6	Cl	15	13	14	321	54.6	568.4
					Al	0.33	0.17	0.08	7.062	0.714	3.249
					Fe	0.32	0.15	0.12	6.849	0.63	4.872
					Mn	0.07	0.05	0.06	1.498	0.21	2.436
HUB-OUT	3975	37.6	7.4	71.5	Cl	9.4	9.2	9.6	353.44	68.08	686.4
					Al	0.22	0.23	0.08	8.272	1.702	5.72
					Fe	0.36	0.07	0.1	13.536	0.518	7.15
					Mn	0.03	—	0.05	1.128	—	3.575
LONG-OUT	4780	45.3	8.9	86	Cl	8.2	—	8.3	371.46	—	713.9
					Al	0.17	—	0.12	7.701	—	10.32
					Fe	0.12	—	0.17	5.436	—	14.62
					Mn	0.03	—	0.04	1.359	—	3.44

*FIL-IN = FIL-3 (inflow from Frederick Lake—see Table 2); FIL-OUT, outflow from Five Island Lake; HUB-OUT and LONG-OUT, outflows from Hubley Big Lake and Long Lake, respectively.

where mass balance studies indicate the partial retention of Al and other elements.[9]

Risk of acid drainage—black slate belts

The part of the Meguma zone shown in Fig. 1 consists largely of Meguma Group metasediments whose upper unit, the Halifax Formation, contains pyritic shales with extensive outcrops east and west of Halifax. The shale is regionally metamorphosed to slate and contains substantial concentrations of As, Sb, W, Fe, Mn and other heavy metals. The Sb map (Fig. 6(*a*)) for centre-lake bottom sediment indicates several areas of enrichment in heavy metals and, therefore, of increased risk over bedrock, including the Halifax Formation, especially around Lunenburg. The As map (Fig. 6(*b*)) shows a similar trend to Sb, with highs over the Meguma Group metasediments. The As map also indicates areas of potential mineralization in the north of the area over granitoid rocks, some of which are known to be hydrothermally altered by mineralizing fluids. As the pyritic slate is exposed to surface weathering the contained As and Sb are also released into the environment, which is indicated by the lake-sediment maps. This illustrates an important point not only for exploration but also for transportation and land-use planning. Strict guidelines for construction are in place for the Halifax Formation slate because of the risk of acidified runoff. Normal construction activities within the Halifax Formation have resulted in increased pyrite oxidation as new rock surfaces are created by standard blasting or excavation techniques. At Soldier Lake an extension of the airport runway in the catchment area resulted in dramatic acidification of the whole lake system.[9] Around Halifax itself the removal of this slate and its use as fill in a separate location have also resulted in increased acidification of the Long Lake system.[27]

Urbanization of watersheds—evidence from lake-sediment cores

Studies at Chocolate Lake[25] have indicated a number of significant chemical changes (Fig. 7). Increasing bedrock exposure, weathering and additions from human activities have resulted from changing land use within the lake catchment. Only a summary of these results will be given here as full details have been provided by Ogden and co-workers.[12]

Increased deposition of the heavy metals Al, As, Fe and Mn has resulted from accelerated excavation and construction activities since about 1950. Anthropogenic input of Cr, Pb, V and Zn is noted and the use of road salt for ice control is indicated by increased levels of halophilous diatoms. Deforestation is indicated by changes in the record of tree pollen and diatoms since about 1750. Increasing lake-water eutrophication due to leaching of domestic waste is reflected in increases in the presence of alkaliphilous diatoms, which show pH changes from approximately 4.5 prior to 1900 to near neutral (pH 7) in the 1970s.[12]

Evidence of climatic change from lake-sediment cores

In all lakes of the St Margarets Bay area the organic–inorganic transition occurred between 10 000 and 11 000 RYBP (radiocarbon years before present), which is consistent with a similar transition observed in cores from other lakes in the Halifax area.[16] The sharp transition is inferred to represent the diversion of glacier melt waters and outwash as the retreating and downwasting ice freed a headwater divide[16] (Fig. 8). In all sediment cores a sterile clay layer 5–15 cm thick reflects the settling of 'rock flour' once the inflow of glacier melt waters had ceased and the lakes began to receive inputs from their own watersheds.[13]

The general increase in organic matter content since *ca* 10 500 RYBP is characteristic of most post-glacial lakes in eastern North America and closely resembles sediment sequences in other lakes of the Halifax area.[16,28] The increase in organic matter is a consequence of decreased soil erosion and increasing vegetational cover as post-glacial climatic warming permitted the re-establishment of closed boreal forests.

A mid-post-glacial (3500–5500 RYBP) warm, dry maximum has been described[29] as the xerothermic interval and has been recognized in Nova Scotia.[16,29] The organic matter maximum in cores (Fig. 8) may represent an interval when reduced precipitation and/or runoff resulted in an apparent increase in organic sedimentation.

In core from Five Island Lake the concentration of Al in

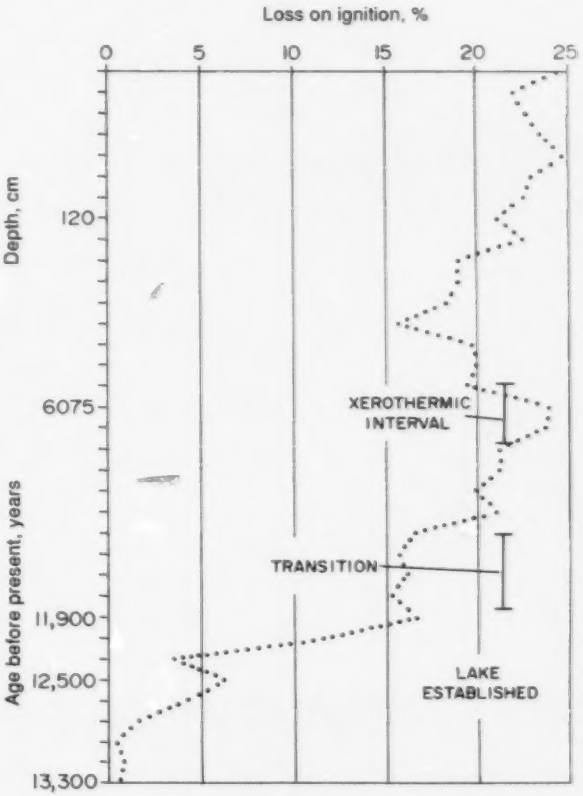

Fig. 8 Organic content of lake-sediment borehole from St Margarets Bay area indicating evolution of catchment by afforestation and evidence for climatic change

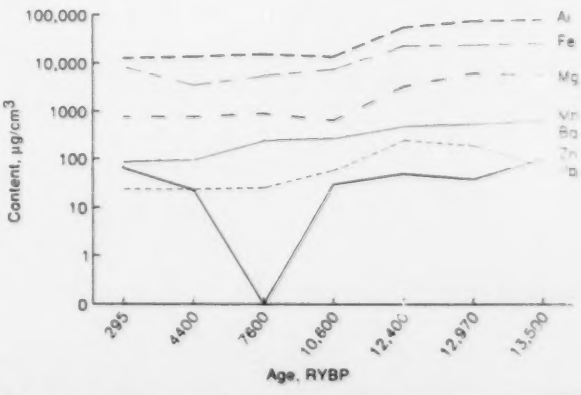

Fig. 9 Chemical trends in lake-sediment boreholes from St Margarets Bay lakes (RYBP, radiocarbon years before present)

the sediment decreases with time since basin formation (Fig. 9). As Al is a major component of soil clay minerals, it is to be expected that its downstream availability should decrease over time as a result of normal processes of weathering, leaching and soil development. Whereas Al seems to reflect consistent processes of soil development, Fe deposition shows an initial response to organic production following the loss of melt water through flow. A maximum at about 10 000–11 000 RYBP is seen for Fe, perhaps coincident with the early development of post-glacial peat bogs. The subsequent decreasing deposition of Fe possibly reflects a decreasing source availability within the watersheds by hydrogeochemical leaching. Manganese and iron have broadly similar depositional patterns, probably reflecting biological mobilization and subsequent soil depletion. The deposition of Mg, Ba and Ca (not shown in Fig. 9) possibly reflects depletion by leaching following isolation of the watershed at *ca* 1000 RYBP. For Zn a decrease since basin isolation is seen, whereas Pb increases in the upper (youngest) composite samples, probably reflecting the use after 1900 of tetraethyl lead in petrol.

Discussion and conclusions

The case studies that have been described show that regional and detailed geochemical studies can be used to detect environmental change in Nova Scotia. One major conclusion is that geochemical exploration in Nova Scotia based on lake sediments must take cognizance of the dramatic differences in deposition after 1950 that have resulted from human activities. The use of lake-sediment cores to establish man-made chemical trends is particularly noteworthy, especially when geochemical methods are being applied to urban areas.[31] It is relevant to note that, on both a regional and global basis, there are no longer 'pristine' environments.

The sedimentary record available from cores in the Chocolate and St Margarets Bay lakes is a necessary adjunct in the preparation of environmental impact assessments. The establishment of natural baselines in North America is possible using lake-sediment cores and should be part of any geochemical mapping exercise.[31] This issue is especially relevant to sampling of the ecological zone or landscape[30] as lake-sediment cores are perhaps unique in providing geochemical, biostratigraphic, temporal and spatial data.[31]

The application of regional stream- and lake-sediment geochemistry to mineral exploration is well documented and this remains the principal use of the data. However, as the Cobequid and Meguma studies show, geochemical surveys can be used to identify potential geological hazards related to particular bedrock units. Data integration using remote sensing and 'Geographic Information System' technology can be used to model and estimate the main geochemical factors.[19] Land-use studies should therefore consider geochemical factors not only for mineral resource purposes but also for potential toxic effects. The elevated levels of heavy metals, such as As and Sb, in the Halifax Formation slate and mineralized areas of granitoid rocks indicate potential problems for water quality and health. The Cobequid Highlands study also indicates a potential problem with Mo as it can cause liver problems in cattle. It is recommended that this area not be used for hay production. Fortunately, the Mo is at present contained by acidified surface waters in immobile complexes, which is perhaps one of the few positive benefits of acid precipitation.[32]

These studies also demonstrate the relationships between connected lake and stream drainage systems and the dynamic nature of their chemical budgets. In the St Margarets Bay lake system it is anticipated that the quality of both runoff and water will be affected as development pressures continue in the watershed. This is relevant to the freeing of alumina and other metals during construction, a process that has resulted in dramatic environmental degradation in a number of lake watersheds of the Halifax area, such as Soldier Lake. With increasing acidification the development of domains of geochemical deposition similar to those observed in Soldier Lake is predicted.

In addition to the positive benefit of acidic water with regard to molybdenum, the Chocolate Lake study highlights the complex interactions that characterize geochemical factors related to human activity. In Chocolate Lake eutrophication from urban or cottage development has adversely affected its recreational and aesthetic properties. On the positive side the enrichment of nutrients in Chocolate Lake has provided an increased buffering capacity against the effects of acid precipitation.

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Geological and metaliogenic aspects of late Variscan Ba–(F)–(base-metal) vein deposits of Spanish Central System

J. Lillo, R. Oyarzun, R. Lunar, M. Doblas, A. Gonzalez and N. Mayor

Synopsis

The central domain of the Spanish Central System contains a series of Ba–(F)–(base-metal sulphide) hydrothermal vein deposits that are hosted by adamellitic granitoids. As a group, these deposits define a northeast–southwest-trending metallogenic province of late Variscan age. Fluid inclusion and sulphur isotope data suggest that the mineralization was formed by low-salinity hydrothermal solutions that incorporated fluids, metals and sulphur from a magmatic source ($\delta^{34}S$ values in barite of +12.27 to +16.59‰ and in sulphides of −4.42 to +0.46‰). This process developed as a consequence of late Variscan magmatism, which triggered hydrothermal activity with major participation by meteoric water. Mineralization occurred in two main stages: a first stage of open-space filling with quartz–Ba–(F)–(base metals); and a second stage of brecciation and deposition of quartz–barite. The two mineralizing events can be clearly related to two tectonic episodes of late Variscan age that involved extension along east–west trends followed by ductile transcurrent movements along northeast–southwest trends.

The Spanish Central System (SCS) is a northeast-trending mountain range located in central Iberia (Fig. 1) and is bounded to the north and south, respectively, by the Tertiary Duero and Tajo sedimentary basins. The SCS belongs to the central Iberian subdivision of the Hesperian Massif[17] and comprises metamorphic complexes of Precambrian/Cambrian age, Ordovician to Silurian metasedimentary sequences, Variscan and late Variscan plutonic rocks (western and central domains of the SCS), late Variscan volcanic rocks (in the easternmost domain of the SCS) and Triassic, Cretaceous and Caenozoic sedimentary rocks.

A significant number of Ba–(F)–(base-metal sulphide) vein-type mineralizations developed within the central domain of the SCS.[21–24,26,35] The present contribution offers a model for these occurrences, suggesting that the deposits formed during a major extensional event that ultimately led to the collapse of the previously overthickened Variscan edifice of central Iberia (late Carboniferous (Stephanian) to Permian).[9,10,11] This event induced widespread magmatic activity, the unroofing of metamorphic core complexes, an increase of the geothermal gradient and high-level hydrothermal activity that included convective systems of meteoric waters.

The deposits (Table 1) define a northeast–southwest-trending Ba–(F)–(base-metal) metallogenic province (Fig. 2). The veins were mined for lead and silver during the late nineteenth and early twentieth centuries, but low grades and rather limited vein widths (<1 m) made exploitation unprofitable. However, the oil exploration boom in the early 1970s led to renewed exploitation, this time for barite. No mine is active at present. There are no precise records of the actual production of these deposits, but examination of the abandoned workings suggests that, at most, a few thousand tonnes was mined from each productive deposit, mostly by trenching along strike and by direct extraction from small galleries.

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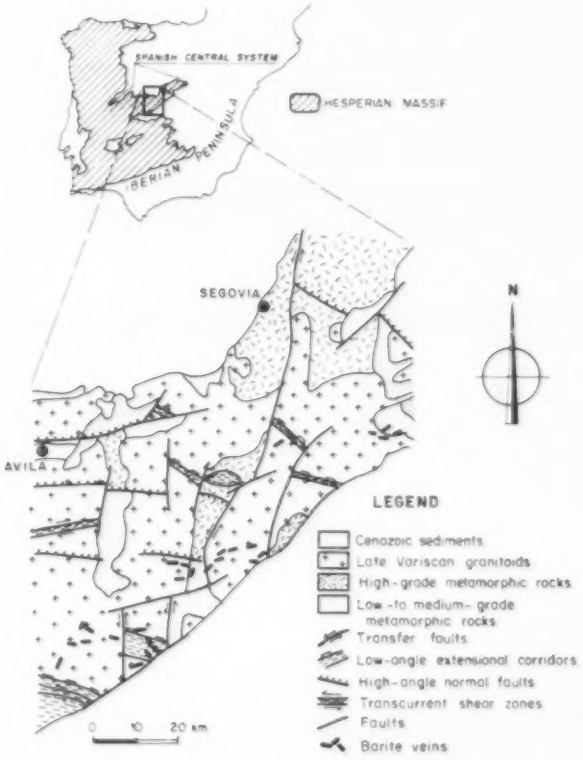

Fig. 1 Generalized geological map of central part of Spanish Central System. (Modified after Doblas *et al.*[11] and Mayor and co-workers[24])

Geological and tectonic framework of central domain of Spanish Central System

The central part of the SCS (Fig. 1) is characterized by: minor outcrops of Variscan palingenetic/synorogenic granitoids that have been variably affected by Variscan tectonometamorphic events; extensive outcrops of late-orogenic and post-orogenic, late Variscan granitoids; metamorphic rocks, including orthogneisses, paragneisses, migmatites and metasediments that have been subjected to polyphase metamorphism; and Caenozoic sedimentary rocks. Outcrops of the granitoids, which are mainly late to post-orogenic, make up most of the central domain of the SCS. The rocks define, as a whole, a composite calc-alkaline trend[12] that consists of gabbros, quartz diorites, tonalites and adamellites (the latter being the host rocks to the Ba–(F)–(base-metal sulphide) mineralization), together with granodiorites